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Description

This invention relates to dental compositions comprising polymerisable material and inorganic fillers.

Many polymerisable materials have been used for dental applications. Examples of materials include polyurethanes, monomeric and polymeric acrylates and methacrylates, polyamides, epoxy-compounds, polystyrenes. Many applications have been envisaged such as fillings, crowns, denture base, coating, sealants and cements. In some of these applications it has been proposed to add inorganic fillers in order to confer desired pigmentation and/or strength.

Preferred polymerisable materials used in dental filling compositions include diacrylate such as the reaction product of Bisphenol A and glycidyl methacrylate, sometimes called bis-GMA as described in United States patent specification 3066112 and such as those described in German Offenlegungsschrift 2816823 and vinyl urethane prepolymer such as those described in British patent specification 1352063. These ethylenically unsaturated materials are polymerised *in situ* using a conventional redox (e.g. amine peroxide) catalyst system or ultra violet preferably visible light catalyst system such as that described in British patent specification 1408265.

Compositions which contain up to about 90% by weight of an inert inorganic filler are described in for example British patent specifications 1465897, 1488403, 1498421, United States patent specifications 3629187 and 3709866, and German Offenlegungsschrift 2419887.

In particular French patent specification 2340085 describes a dental filling composition containing a filler in which 70% to 95% by weight of the particles have size 0.7 to 24 microns and 30% to 5% by weight of the particles have size 0.2 to 0.7 micron. The specification states that filler having a smaller particle size must not exceed 5% by weight of total filler because of attendant decrease in compressive strength. German Offenlegungsschrift 2405578 describes the use of filler having particle size less than 0.07 micron, preferably as sole filler, in a dental filling composition. Small quantities of a larger particle size filler may apparently be tolerated.

There has however been a requirement for a considerable time for a polymerisable material-based composite which when cured has physical properties particularly wear and tensile properties similar to or better than amalgam.

It has now been found that inclusion of a mixture of inorganic fillers having certain selected range of particle size and concentration in the composition provides for example a dental composite having such a desirable compromise of physical and aesthetic characteristics. PCT application 81/00031 describes dental filling compositions containing fine particle size filler and a minor amount of large particle size filler; however that fine particle size filler is said to be hydrophobic whereas such fillers in the present invention for example 'Aerosil' OX 50 and 'Aerosil' A130 are hydrophilic.

According to the present invention therefore a fluid dental composition is provided which comprises liquid polymerisable material (A), filler (B), polymerisation catalyst for the polymerisable material and dispersing agent, characterised in that the filler is a mixture of fillers in volume fraction from 60% to 85% where volume fraction is expressed as

$$\frac{(\text{volume B} \times 100)}{(\text{volume A} + \text{volume B})}$$

said mixture of fillers comprising fine particle size filler and large particle size filler, the fine particle size filler having a mean size value in the longest direction of less than 0.1 μm. and being present in volume fraction from 10% to 55% where volume fraction is expressed as

$$\frac{(\text{volume fine} \times 100)}{(\text{volume A} + \text{volume fine})}$$

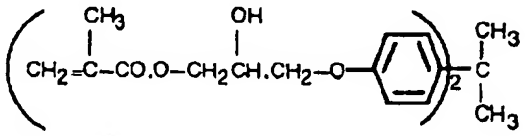
and the large particle filler having the mean size value in the longest dimension of 0.5 μm. to 80 μm.

By the term fluid is meant a range of viscosity for example sufficiently stiff at ambient temperature to enable the composition used as a filling material to be applied to a tooth cavity in a coherent mass but not having so low a viscosity that the composition flows readily from the tooth cavity and for example when used as a glaze a viscosity sufficient for flow over a tooth surface. By the term liquid, applied to the polymerisable material is meant such viscosity at ambient temperature as will make, with any other liquid additives, e.g. (c) and (d), the composition fluid without the polymerisable material having undue volatility.

The polymerisable material may be any liquid ethylenically unsaturated polymerisable resin suitable for dental applications. Preferably the material is a diacrylate or dimethacrylate. Typical of such materials are those hereinbefore described. Most preferred materials are vinyl urethanes such as for example those described in British patent specifications 1352063, 1465097, 1498421 and German Offenlegungsschrift 2419887 or the reaction product of a diol such as a glycol but particularly a bisphenol with a glycidyl alkacrylate such as those described for example in United States patent specifications 3066112, and 4131729 (the disclosures

in these specifications are incorporated herein by way of reference).

A preferred reaction product of a glycidyl alkacrylate and a diol has the formula:



Preferred vinyl urethanes described in the aforesaid British patent specification and German offenlegungsschrift are the reaction product of a urethane prepolymer and an ester of acrylic or methacrylic acid with a hydroxy alkanol of at least 2 carbon atoms, the urethane prepolymer being the reaction product of a diisocyanate of the structure OCN-R^1-NCO and a diol of the structure HO-R^2-OH wherein R^1 is a divalent hydrocarbyl group and R^2 is the residue of a condensate of an alkylene oxide with an organic compound containing two phenolic or alcoholic groups.

Other suitable vinyl urethanes include those made by the reaction of alkyl and aryl, preferably alkyl, diisocyanates with hydroxy alkyl acrylates and alkacrylates such as those described in British patent specification 1401805, 1428672 and 1430303 (the disclosure of which are included herein by way of reference), vinyl maleate urethanes and vinyl isocyanurates.

The polymerisable materials may be a solid or semi-solid and as the siliceous material is also solid it is often necessary (in order to produce a composition which is fluid) to add to the composition sufficient copolymerisable liquid ethylenically unsaturated monomer to make the composition fluid, and in particular to give the composition a cohesive paste-like consistency without being too runny. If desired, the composition may include liquid copolymerisable ethylenically unsaturated monomer even where all the polymerisable components are liquid. The term liquid polymerisable material includes a mixture of such solid or semi-solid with liquid copolymerisable monomer.

Hence the dental composition may contain a mixture of liquid copolymerisable ethylenically unsaturated monomers and should contain such a liquid monomer when the other monomer is a solid in order that the dental filling composition be fluid and in particular have a paste-like consistency.

The amount of such ethylenically unsaturated monomer used may desirably be just sufficient to achieve the desired fluidity in the dental filling composition. It is preferred to use in the present composition between 25% and 150% of ethylenically unsaturated monomer by weight of polymerisable prepolymer.

Suitable liquid copolymerisable ethylenically unsaturated monomers, the polymers of which should be water insoluble, include vinyl monomers, e.g. vinyl esters such as n-hexyl, cyclohexyl and tetrahydrofurfuryl acrylates and methacrylates. The monomers should be non-toxic.

Polyfunctional vinyl monomers, that is, monomers containing two or more vinyl groups are also suitable. Suitable monomers include, for example, glycol dimethacrylates, diallyl phthalate and triallyl cyanurate. Indeed such monomers may if they possess exceptionally low volatility and odour be used as the only polymerisable material in the present composition.

The compositions of the present invention contain filler in volume fraction (V fill) from 60% to 85%, preferably 60% to 75% where

$$V\,fill = \frac{F}{P+F} \times 100$$

in which F is the total volume of filler and P is the volume of polymerisable material.

The filler comprises a mixture of fine particle size filler and large particle size filler. The fine particle size filler (FF) is present in the composition in volume fraction (V_{FF}) from 10% to 55%, most preferably 10% to 25% where

$$V_{FF} = \frac{\text{volume FF} \times 100}{P + \text{volume FF}}$$

By fine particle size filler is meant a filler having a mean size value in the longest dimension of less than 0.1 μm; commonly the surface area of fine particle size filler will be 40 to 300 m^2/g. It may be for example any form of silica including comminuted forms of crystalline silicas including for example sand, but is preferably a colloidal form for example a pyrogenic or fumed silica, or a precipitated silica. The fine particle filler may also be for example titanium dioxide, aluminium oxide or a radio-opaque filler and mixtures thereof.

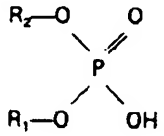
The mixture also contains large particle size filler (LF) having a mean size value in the longest dimension of 0.5 μm to 80 μm, preferably less than 55 μm and most preferably less than 30 μm and desirably containing less than 5% by volume of particles having mean size value of more than 80 μm. The large particle size filler may have a smooth distribution of particle size value but may show a single peak at the mean value or that

filler may comprise a mixture of fillers which may in particle size distribution show two or more, but preferably two, three or four peaks in a distribution of particle size value within the range.

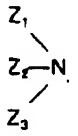
The large particle size filler may also be siliceous such as for example silica in the form of fine sand and other crystalline quartz, but may also be any suitable silicate glass such as for example barium aluminium silicate, or a glass incorporating a rare earth or other suitable oxide such as lanthanum, strontium, tantalum, zirconium, gadolinium, dysprosium, hafnium, or tungsten oxide and other fillers such as alumina, titanium dioxide calcium fluoride so as to impart a desired property such as radio-opacity, refractive index and hardness. However, choice of filler may depend upon other features of the present composition such as desired colour for matching existing teeth and the type of catalyst being incorporated. It may be desirable for the composition to include a radio-opaque filler because the dentist can more easily ascertain the location and anatomic form of the composition within a cavity.

In order to assist with incorporation of the filler in the preparation of the present composition, a dispersing agent is required in particular in conjunction with the fine particle size filler. Incorporation may also be assisted by the use of a diluent e.g. methylene chloride but such a diluent will generally require subsequent removal.

A preferred dispersing agent for the fine particle size filler contains a mixture of compounds comprising a phosphorus oxyacid having the formula:-



wherein R_1 is an organic group containing a terminal chain which is either a hydrocarbon group having at least six carbon atoms or a polyether or polyester of molecular weight greater than 200 preferably from 500-10,000, R_2 is either a group as specified for R_1, a hydrogen atom, or a hydrocarbyl or substituted hydrocarbyl group not having a terminal chain of at least six carbon atoms and an organic base nitrogen compound having the formula:-



wherein Z_1 is a group as specified for R_1 above and Z_2 and Z_3 which may be the same or different are as specified for R_2 above.

The molar proportion of acids to bases in the above dispersing agent may be from 0.5:1 to 100:1 but it is better to have an approximately 50% molar excess of acid present and therefore preferred proportions are from 1:1 to 3:1 measured as molar ratios of acid to base.

The weight concentration of the dispersing agent in the composition of this invention is not critical but should be related mainly to the weight of the filler mixture present in the composition. The concentration of acid and amine in the composition should generally be in the range separately 0.1% to 5% by weight relative to weight of filler mixture. For best results a concentration of less than 10% by weight of the dispersing agent is preferred.

Dispersions of fine particle size filler in organic media including a dispersing agent based on the above acids and amines are described in European Patent Application A1-3491A1, the disclosure of which is included herein by way of reference. The dispersions are said to be useful as dental filling materials but those containing fine particle size filler above are described.

It is desirable, particularly at higher levels of filler loading to use a dispersing agent in conjunction with inclusion of large particle size filler. The dispersing agent assists in maintaining fluidity of the composition. Preferred dispersant for the large particle size filler are polymeric dispersants such as those described in British patent specification 1493393, the disclosure of which is incorporated herein by way of reference. The amount of such dispersant to be used varies widely depending upon for example the chemical structure of the dispersant, the type and particle size of the filler and the polymerisable material.

The particle size of the large particle size filler may if desired be reduced before incorporation with the other ingredients to form the present composition, by for example dry milling. The filler so milled or as supplied may then be pre-mixed with any dispersant and some of the other ingredients of the composition before all

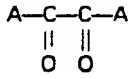
the components of the composition are finally mixed.

The dental compositions of the present invention include free radical generating systems. These include those based on a catalyst such as for example organic peroxide and an accelerator such as an organic amine as described in some of the aforementioned specifications. Also included are those catalyst systems which are sensitive to ultra violet radiation such as those based on monoketones, hydroxy ketones and their alkyl esters. Preferably the catalyst is activated by visible light for example those described in British patent specification 1408265 and Belgian patent 789950, the disclosures of which are incorporated herein by way of reference. These catalysts comprise a photo sensitiser and a reducing agent capable of reducing the photosensitiser when the latter is in an excited state.

The dental compositions of the present invention may depending upon the catalyst incorporated therefor be cured for example by irradiating the compositions with ultra violet radiation, that is, with radiation having a wavelength in the range about 230 μm up to 400 μm. The compositions may also be, and preferably are, cured by irradiating with visible radiation having a wavelength in the range 400 mμ to 500 mμ. Alternatively, a mixture of ultra violet and visible radiation may be used.

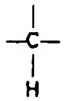
Suitably the concentration of the photosensitiser is 0.001 % to 10% by weight, preferably 0.1 % to 5% by weight and the concentration of reducing agent is similar but preferably is 0.25% to 5% by weight, most preferably 0.25% to 1.00% by weight, all these percentages being by weight of the polymerisable material in the dental composition.

A preferred photosensitiser is selected from fluorenone, substituted derivatives thereof, and α-diketones having the structure:



in which the groups A, which may be the same or different, are hydrocarbyl groups or substituted hydrocarbyl groups including camphorquinone.

Preferred reducing agents are selected from those having the structure R_3N where the units R, which may be the same or different, are hydrogen atoms, hydrocarbyl groups, substituted hydrocarbyl groups or groups in which two units together with the nitrogen atom form a cyclic ring system, no more than two of the units R being hydrogen atoms and, where the nitrogen atom is attached directly to an aromatic group R, at least one of the other units R has a



In order that a dental filling composition may be produced in which the siliceous filler in the composition adheres particularly well to the polymerisable material it is much preferred that the filler be treated with a coupling agent which is capable of reacting with both the siliceous particles and the polymerisable material before the mixing of the filler and polymerisable material is effected. The coupling agent should have the effect of increasing the strength of the bond between the filler and the cured polymerisable material in the filling.

Suitable coupling agents especially for use with glass or silica include silanes, e.g. γ-methacryloxypropyltrimethoxysilane, γ-aminopropyltriethoxysilane and γ-glycidoxypropyltrimethoxysilane.

Mixing of the polymerisable material with the filler and other ingredients to form the present dental filling composition may be effected by simply stirring the ingredients together. However as the polymerisable material optionally including copolymerisable monomer may be viscous and thus difficult to stir with the filler so as to achieve adequate mixing, the polymerisable material optionally including copolymerisable monomer may conveniently be diluted with a suitable diluent so as to reduce the viscosity thus enabling adequate mixing of the filler to be more readily achieved. When mixing has been effected the diluent may be removed, e.g. by evaporation. Suitably, the diluent may be the copolymerisable ethylenically unsaturated monomer above, the level of the other monomer subsequently being reduced to the desired extent.

However it is preferred that some of the ingredients be premixed in order to facilitate more thorough final mixing of all the ingredients. For instance the fillers are preferably separately mixed with any dispersing agent and some of the polymerisable material, and as desired in an inert diluent so that the filler is thoroughly wetted. Such a mixture incorporating a large particle size filler may be milled so as to reduce particle size of the filler

before addition to the main bulk of the eventual mixture.

After mixing together all the ingredients of the present composition, any diluent which is not required for subsequent curing should be removed for example by evaporation preferably under reduced pressure so as to facilitate removal at nearer to ambient temperature and to reduce the level of air in the final mixture. Any mixing or manipulation of the mixture which includes polymerisable material and ultra violet or visible light sensitive catalyst should be carried out in substantial absence of such radiation in order to avoid premature cure. Also, where the catalyst system comprises two components such as peroxideamine which when mixed together produce curing those two components should not be added together to the mixed bulk of the other ingredients but one such component to one half of the bulk and the other such component to the other half of the bulk.

Whilst it is primarily envisaged that the compositions of the present invention will be useful as dental filling materials, they may also be useful as dental glazes and veneers, orthodontic adhesives, denture base and for artificial teeth crowns and bridges. In particular the composition should have a stiff paste or doughy consistency if it is to be used as a filling material; it should be a liquid preferably flowable if it is to be used as a dental glaze so that it may be applied to the prepared tooth surface e.g. by brushing and therafter flow before curing so as to produce a smooth surface. If the composition is to be used as an orthodontic adhesive, then a wide range of consistency is envisaged depending on what is to be adhered to the tooth and the way in which the adhesive is to be applied; for example where a dental bracket is to be adhered to a tooth the composition may be a liquid so that it may be applied to the tooth and the bracket pressed into the liquid film or the composition may be a dough which is applied to the back of the bracket or to a small area of the tooth surface before mating the tooth and bracket. Accordingly the present composition is coherent and not crumbly or powdery.

Where the dental composition of the present invention contains a catalyst activatable by ultraviolet or more particularly visible light, it may conveniently be packed in small containers (e.g. 10 g. capacity) or unit dose form so as to facilitate handling in the surgery and to reduce the risk of inadvertent curing by U.V. radiation or stray light. However, where the catalysts consists of two components which react when mixed as in for example peroxide-amine combinations, the present composition is preferably packed in two containers, one containing peroxide and the other the amine, together with such other components of the mixture such that when the contents of the two containers are mixed, e.g. in a dentist surgery, the present composition is produced.

For cosmetic purposes the present composition may have a flash coloured (for dental base) or natural tooth appearance, and hence the present composition may include small quantities of pigments, opalescent agents and the like. The composition may also include small quantities of other materials such as anti-oxidants and stabilisers provided that they do not substantially affect the cure.

It is preferred that the surface of the tooth be cleaned before application of the composition. The tooth may be so cleaned by for example grinding with a rotating wheel or brush or by etching using for example aqueous phosphoric acid. For complex cavity work, etching and bevelling of enamel margins may improve retention and anatomic form of the composite restoration, particularly if used in conjunction with a bonding agent (e.g. unfilled polymerisable material). The dental composition may be applied to the tooth, e.g. as a filling to a cavity in the tooth, and the polymerisable material is then polymerised so that the composition is formed into a hard material. When used as a dental filling material it is preferred that a cavity liner is first applied. The liner may be any normally used in the composite filling art such as polycarboxylate and calcium hydroxide aqueous slurry cements. Suitable lining cements are described in Journal of Dentistry, Vol. 6 No 2, 1979, pages 117-125. In general it is preferred to avoid liners such as zinc oxide-eugenol liners which may interfere with the curing of the composite.

The invention is illustrated with reference to the following Examples:-

Example 1

Condensate (35.2 g, 0.1 mole) obtained by reacting 2,2-bis-(4-hydroxyphenyl)propane and propylene oxide in a molar ratio of 1:2 (oxypropylated Bisphenol A) was dissolved in approximately 100 g of methylene dichloride and the resulting solution was added dropwise to a solution of 33.6 g (0.2 mole) of hexamethylene di-isocyanate in 100 g of methylene dichloride under an atmosphere of nitrogen gas. 4 drops of dibutyl tin dilaurate (available as "Mellite" 12, "Mellite" is a registered Trade Mark) were added as catalyst. The mixture was stirred under nitrogen for 1 hour after which it was heated under reflux conditions for 9 hours. The mixture was then cooled and a solution of 29 g (0.2 mole) of hydroxypropyl methacrylate in 100 g of methylene dichloride was added after which the mixture was heated under reflux conditions for 3 hours. The hydroxypropyl ester comprised isomers in weight ratio 2-hydroxypropyl (2.6 parts) to 1-methyl-2-hydroxyethyl (1 part). The mixture of vinyl urethane and methylene chloride was then cooled. Dimethyl long-chain alkyl tertiary amine (0.6 g Ar-

mour Hess Armeen DM 16D), di-(2-ethylhexyl) phosphoric acid (1.00 g.) and methacryl silane (1.33 g. Union Carbide Corporation grade A 174) were added to the mixture. Fine particle size filler (Aerosil A 130); mean size value 0.02 µm) was then stirred in amount appropriate to the level required in the final composition together with triethylene glycol dimethacrylate in weight amount the same as the vinyl urethane.

Large particle size fillers (LF) were prepared by milling in methylene chloride (50:50 by volume) which contained silane (A 174) 2% w/w on filler and water (0.2% w/w on filler). One mixture (LF_1) had filler mean size value 3.8 µm and the other mixture (LF_2) had value 2.5 µm.

To each mixture was added camphorquinone (0.75% by weight of polymerisable material) and dimethylaminoethyl methacrylate (0.5% by weight of polymerisable material). Methylene chloride was removed by stirring at ambient temperature followed by vacuum evaporation.

Samples of the resulting dispersions which were fluid paste compositions were charged to polyethylene moulds of (1) length 2.5 mm and diameter 3 mm and (2) length 25 mm and square (2 mm side) cross-section. Curing was effected by 1 minute exposure of the total sample under test to light from the end of Quartz optic light guide length 11 cm. diameter 8 mm. coated along its length with a Netlon sleeve (trade mark) and shrink wrap coating of polyvinyl chloride. The light source was a tungsten halogen lamp 12 volt, 75 watt, (Thorn Electrical A.1/230) fitted with an ultra violet filter. Physical properties of the cured moulded samples were then determined-samples (1) for Compressive strength and Diametral Tensile Strength and samples (2) for Flexural Strength after sample immersion in deionised water at 37°C for 72 hours.

		A	B	C	D	
FF	Filler by volume	20	10	22	—	
LF_1		70	67	46	100	
LF_2		10	23	32	—	
VFF		26.3	14.2	32.4	—	
VLF		59.1	59.3	62.9	64.0	
V_{mix}		64.3	61.9	68.5	64.0	
						Amalgam
Flexural Strength (MN m^{-2})		85	121	131	131	
Diametral Tensile Strength (MN m^{-2})		37	45	53	50	47
Compressive Strength (MN m^{-2})		236	234	256	287	350
Wear ratio (After 501 hours)		1.03	1.09	0.36	4.76	1.00

Wear strength was evaluated by the method described in J. Biomed. Mater. Res., (1975) Vol. 9 Pages 341 to 353 and are expressed as ratios compared to wear of amalgam.

The results show that the compositions of the present invention containing a mixture of particle size filler have similar physical properties to amalgam and much improved wear characteristics to compositions containing large particle size filler alone.

Example 2

A dental composition was prepared using the same vinyl urethane as that in Example 1. A resin mixture was prepared comprising vinyl urethane (50 g) triethylene glycol dimethacrylate (50 g including 10 ppm hydroquinone), camphorquinone (0.75 g), dimethylaminoethyl methacrylate (DMAEM 1 g), ultra violet stabiliser (0.5 g; "Tinuvin" 326; Ciba-Geigy Ltd.), antioxidant (1 g; "Irganox" 1010 Ciba-Geigy Ltd.).

Filler A was prepared by wet milling sodium borosilicate glass, resin mixture (34% by weight of glass and resin), methacryl silane (A 174, Union Carbide Corporation, 1% w/w glass), copolymer dispersant and methy-

lene chloride (30% by weight of the filler and resin) until the filler mean size value was 1.5 µm. Particle size distribution is shown in Figure 1. The mixture was stirred in a dough mixer until almost all (about 97% by weight) of methylene chloride had been removed and finally milled under vacuum to reduce substantially the methylene chloride content.

Filler B was prepared by dry milling sodium borosilicate glass until the filler mean size value was 5 µm. Particle size distribution is shown in Figure 2. The glass was mixed with a methanol/methylene chloride/water solution (40% w/w on glass; 10/30/1 component proportion) to form a slurry. To the slurry was added methacryl silane (1% w/w on filler, Union Carbide Corporation, Grade A 174) with stirring. The glass was then filtered off and the filter cake was dried in an oven.

Filler C was prepared by mixing Aerosil OX50 (mean size value 0.02 µm), resin mixture (about 62% w/w on Aerosil and resin), methacryl silane (2.3% w/w on Aerosil; Union Carbide Corporation, Grade A 174), di(2-ethyl hexyl)phosphoric acid (DEHPA; 2.1 % w/w on Aerosil), (C_{12-14}alkyl)dimethyl amine (Albright and Wilson Ltd., 1.2% w/w on Aerosil in a dough mixer). The resultant mixture was then milled under reduced pressure to remove the air.

A mixture was then prepared by mixing portions of resin mixture and Fillers A, B and C to produce a dental composition comprising:-

	Weight (g)	Origin
Vinyl urethane	8.67	some Filler A some Filler C
Triethylene glycol dimethacrylate	8.67	most resin mixture
Fine Particle size filler	7.97	Filler C
Large Particle size filler	7.74	Filler A
Large Particle size filler	65.52	Filler B
Silane	0.26	Fillers A+C
DEHPA	0.17	Filler C
Amine	0.09	Filler C
Copolymer dispersant*	0.16	Filler A
Antioxidant	0.17	Resin mixture
U.V. Stabiliser	0.09	Resin mixture
DMAEM	0.17	Resin mixture
Camphorquinone	0.13	Resin mixture
Water	0.17	

The volume fractions of the filler were:-

V_{fl}=69.6% V_{FF}=18.5%; V_{LF} (Filler A)=17.9%; V_{LF} (Filler B)=65.8%.

In order to assist mixing, a small quantity of methylene chloride was added. After mixing on a dough mixer, the mixture was then milled under reduced pressure to remove air and the methylene chloride. All the mixing procedures above which involved resin in the presence of camphorquinone and DMAEM were carried out under sodium vapour discharge lamp (yellow light) so as to avoid premature cure of the resin.

Test pieces were prepared as described in Example 1 from samples of the composition and gave the following results (sample water immersion-24 hours):-

Flexural Strength	140 MN/m²
Diametral Tensile Strength	52 MN/m²
Compressive Strength	321 MN/m²

Wear ratio (after 261 hours)	0.80
Knoop Hardness	81

A similar composition which was radio-opaque was prepared in which barium aluminium borosilicate glass replaced on an equal volume basis all the sodium borosilicate glass in Fillers A and B above.

Particle size distribution of Filler A and B were determined by sedimentation techniques using Sedigraph 5500L (Micromeritics Limited). Specimens for examination were prepared from samples of the fillers as prepared in methylene chloride (Filler A) and methanol/methylene chloride/water (Filler B) to which further quantities of methylene chloride were added to give required translucency. Resultant distributions are given in Figures 1 and 2 respectively, the equivalent spherical diameter at the 50 Cumulative area percent position being taken as the filler mean size value.

The copolymer dispersant was 95:5 weight ratio copolymer of methyl methacrylate and dimethylaminoethyl methacrylate, M 50,000 (G.P.C.).

For comparison a similar formulation was prepared but containing as filler only fine particle size filler C as follows:-

Vinyl urethane	16.74
Triethylene glycol dimethacrylate	16.74
Fine particle size filler	62.96
Silane	1.47
DEHPA	0.84
Amine	0.74
DMAEM	0.17
Camphorquinone	0.25

V_{FF}=47.7%

The above composition produced test pieces having

Flexural Strength	131.1 ±10.6 MN/m²
Flexural Modulus	9.24±0.6 GN/m²
Wear ratio (100 hours)	4
Wear (100 hours)	155.6 µm

Example 3

A number of compositions were prepared using the procedure described in Example 2 but based on the following composition in order to examine a range of visible light cure catalysts.

	Weight (g)
Vinyl urethane	8.70
Triethylene glycol dimethacrylate	8.70
Filler A	7.80
Filler B	65.51
Filler C	8.021
Silane	0.265
DEHPA	0.107
Amine	0.094
Antioxidant	0.054
U.V. Stabiliser	0.027
Water	0.017
Methacrylic acid	0.315 (added to the resin mixture
Copolymer dispersant	0.162

Catalyst-see following table

The volume fractions of the filler were:-

V_{fill}=69.4% V_{FF}=18.3% V_{LF} (Filler A)=17.9% V_{LF} (Filler B)=64.7%

In preparing the compositions the ketone given in the following table was added to the composition at the same stage as camphorquinone in Example 2. The ketone and amine concentrations were 0.75 and 0.5 respectively expressed % weight on vinyl urethane and triethylene glycol dimethacrylate.

Catalyst		Cure time (s)	Flexural strength (MN/m^2)	Flexural test	
Ketone	Amine			Modulus (GN/m^2)	Length of sample cure(s)
camphorquinone	DMAEM	10	143±12	16.3±0.7	30
benzil	DMAEM	100	110±5.8	10.2±0.6	120
camphorquinone	N-ethyl morpholine	20	123±10.2	15.6±0.9	30
camphorquinone	C_{12} alkyl dimethyl amine "Armeen"	35	127±10.7	14.4±0.7	60
acenaphthene quinone	DMAEM	40	132±10.8	13.2±0.5	60
benzoin	DMAEM	cured on standing			
benzophenone	DMAEM	>500			

*irradiated without ultra-violet filter.

Cure time was determined by the following procedure:-

A 1 g sample of the composition was placed between the plattens of an oscillating rheometer of the type

prescribed in British Standard 5199:1975 but modified by the provision of an aperture in the upper platten through which the composition could be exposed to the appropriate radiation needed to cure the composition. The lower platten of the rheometer was then oscillated relative to the upper platten and the oscillations were recorded automatically. The sample was allowed to equilibrate, and then the radiation was switched on. The time taken for the oscillations to cease was recorded. The results were expressed as the time taken, for a sample 2.1 mm thick to become fully cured.

Example 4

A sample of the composition described in Example 3 but not containing light cure catalyst was divided into two parts. To one part was added

Benzoyl peroxide	0.99
"Topanol" OC	0.02

To the other part was added

N,N-bis-(-2-hydroxylethyl-p-toluidine)	0.52
"Topanol" OC (T.M. ICI Limited)	0.02

The above concentrations are expressed as weight per hundred parts by weight of composition. Equal portions from each part containing the above additives were thoroughly hand mixed. The resultant mixture had a working time 3.5 m (time after mixing until significant increase in viscosity) and a setting time 5 m (time from significant increase in viscosity to setting as judged by zero oscillation on a Wilson Rheometer). Cured samples (after 24 hour water immersion) had

Flexural strength	120±8.5 MN/m²
Flexural modulus	15.3±0.5 GN/m²

as measured according to British Standard 5199:1975 and a wear ratio of about 0.8.

Example 5

A composition was prepared using the procedure described in Example 2 except that Bis-GMA was used in place of vinyl urethane and that the component concentrations were as follows:-

	Weight (g)
Bis-GMA ("Nupol" 46—4005)	8.5176
Triethylene glycol dimethacrylate	8.5176
Filler A	7.8637
Filler B	66.1353
Filler C	8.1022
Silane	0.2656
DEHPA	0.1085
Amine	0.0944
Copolymer dispersant	0.1594
Water	0.0169
Camphorquinone	0.1424
DMAEM	0.0764

("Nupol"-trade mark, Freeman Chemicals Corporation, Port Washington, Wisconsin, U.S.A.). The above composition had the following performance:

	Cure time	20 s
	Flexural Strength	135.5±14.9 MN/m²
	Flexural modulus	17.3±0.73 GN/m²
	Wear ratio	0.8
	V_{fill}=70.1%	
	V_{FF}=18.8%	
	V_{LF} (Filler A)=18.3%	V_{LF} (Filler B)=65.4%

Example 6

A resin mixture was prepared by mixing at ambient temperature triethylene glycol dimethacrylate (TEGDM); 100 g including 10 ppm hydroquinone), camphorquinone (0.75 g), dimethylaminoethyl methacrylate (DMAEM 0.5 g).

Large filler was that described as Filler B in Example 2 except that the filler was barium borosilicate ("Raysorb", Owens-Illinois). Fine filler mixture was prepared as described for Filler C in Example 2 except that the above resin mixture was used and DEHPA concentration was 1.35% w/w on Filler C.

A mixture was then prepared by the procedure described in Example 2 to produce a dental composition comprising:-

	Weight (g)	Density (g/ml)	Origin
Triethylene glycol dimethacrylate	10.77	1.072	
Fine filler	22.09	2.2	
Large filler	65.94	3.09	
Silane	0.517		Fine filler
DEHPA	0.297		Fine filler
Amine	0.253		Fine filler
DMAEM	0.055		Resin
Camphorquinone	0.077		Resin

The volume fractions of the filler were:-

V_{fill}=75.7%

V_{FF}=50.0%

V_{LF}=68.0%

The above composition had the following performance compared with amalgam ("Amalcap", Vivadent)

	Composition	Amalgam
Flexural strength (MN/m²)	146±12.8	75.5±7.7
Flexural Modulus (GN/m²)	24.3±0.49	33.6±6.5
Compressive strength (MN/m²)	376±23.6	—
Wear ratio	0.63	1.00
Diametral tensile strength (MN/m²)	47.1±1.8	—

Example 7

For comparison purposes, a composition was prepared according to the procedure of Example 6 but using the resin mixture described in Example 2 and a different filler level. The formulation was:-

	Weight (%)
Resin mixture	21.66
Fine filler	3.99
Large filler	74.08
Camphorquinone	0.16
DMAEM	0.11

The volume fractions of the filler were:-

V_{fil} 56.3%
V_{FF} 8.3%
V_{LF} 54.45%

The above composition had the following performance:

Flexural strength (MN/m^2)	121±12.4
Flexural modulus (GN/m^2)	11.9±3.0
Compressive strength (MN/m^2)	270±13.2
Diametral tensile strength (MN/m^2)	50.9±5.1
Wear ratio	4
Wear (100 hours)	154.8 µm

Physical properties on cured moulded samples in the above Examples were determined on a Howden Testing Machine-Type EU5BS as follows:-

1. Flexural Strength and Flexural Modulus. After immersion in deionised water for 24 hours (except Example 1) at 37°C, the samples were dried with tissue paper and allowed to equilibrate at room temperature for 10 minutes. Rough edges on samples were carefully sanded down using emery cloth grade O. Cross-sectional dimensions were determined on each sample using a micrometer. Three point bend test was then carried out on each sample using a 200N load cell and a cross-head speed of 1.0±0.05 mm/minute. The load at failure was recorded and flexural strength (FS) calculated according to the following formula:-

$$FS = \frac{3PL}{2bd^2} N/mm^2$$

where

P is the load at failure (N)
L is the distance between supports (mm correct to 0.01 mm)
b is breadth of sample (mm correct to 0.01 mm)
d is depth of sample (mm correct to 0.01 mm)

Flexural modulus (FM) was calculated according to the following formula:-

$$FM = \frac{P^1L^3}{4bd^3y} N/mm^2$$

where Lbd are defined above, y is the centre point deflection (mm) of the beam on the testing machine and P^1 is the load on the linear portion of the load deflection corresponding to the deflection y.

2. Compressive strength. After immersion in deionised water for 24 hours (except Example 1) at 37°C, the samples were dried with tissue paper and allowed to equilibrate at room temperature for 10 minutes. The diameter was measured with a micrometer; each sample was mounted in the upright position between parallel plattens of the testing machine and tested under compression until failure. The load at failure (P measured in Newtons) was recorded and compressive strength (CS) calculated according to the formula:-

$$CS = \frac{P}{\pi r^2} N/mm^2$$

where r is the radius of sample cross-section (measured in mm correct to 0.01 mm).

3. Diametral tensile strength. After immersion in deionised water for 24 hours at 37°C, samples were dried with tissue paper and allowed to equilibrate at room temperature for 10 minutes. The length and diameter of each sample was measured using a micrometer. Each sample was placed on its side between parallel plattens of the testing machine and tested under compression of 1.0±0.05 mm/min; the load at failure (T measured in Newtons) was recorded and diametral tensile strength (TS) calculated according to the formula:-

$$TS = \frac{2T}{\pi DL} N/mm^2$$

where D and L are the diameter and length respectively of the sample (measured in mm correct to 0.01 mm).

In evaluating each property above, the result from 12 samples was averaged, and any value which fell more than 15% below the average was discarded. The mean of the remaining samples was recorded with a standard deviation. The tests were repeated if more than 3 samples were discarded.

In this specification, "Aerosil", "Armeen", "Irganox", "Nupol", "Raysorb", "Tinuvin" and "Topanol" are registered Trade Marks in all of some of the designated contracting states.

Claims

1. A fluid dental composition which comprises liquid polymerisable material (A), filler (B), polymerisation catalyst for the polymerisable material and dispersing agent, characterised in that the filler consists essentially of a mixture of inorganic fillers in volume fraction from 60% to 85% where volume fraction is expressed as

$$\frac{(\text{volume B} \times 100)}{(\text{volume A} + \text{volume B})}$$

said mixture of fillers comprising fine particle size filler and large particle size filler, the fine particle size filler having a mean size value in the longest direction of less than 0.1 µm. and being present in volume fraction from 10% to 55% where volume fraction is expressed as

$$\frac{(\text{volume fine} \times 100)}{(\text{volume A} + \text{volume fine})}$$

and the large particle filler having the mean size value in the longest dimension of 0.5 µm. to 80 µm.

2. A fluid dental composition according to claim 1 characterised in that the filler volume fraction is from 60% to 75%.

3. A fluid dental composition according to either claim 1 or claim 2 characterised in that the volume fraction of fine particle size filler is from 10% to 25%.

4. A fluid dental composition according to any one of claims 1 to 3 characterised in that the fine particle size filler is colloidal or precipitated silica.

5. A fluid dental composition according to any one of claims 1 to 4 characterised in that the large particle size filler shows a single peak in distribution of particle size.

6. A fluid dental composition according to any one of claims 1 to 4 characterised in that the large particle size filler shows two peaks in distribution of particle size.

7. A fluid dental composition according to any one of claims 1 to 6 characterised in that the liquid polymerisable material comprises at least one diacrylate or dimethacrylate ester.

8. A fluid dental composition according to claim 7 characterised in that the liquid polymerisable material comprises a mixture of vinyl urethane and a glycol dimethacrylate.

9. A fluid dental composition according to claim 7 characterised in that the polymerisable material comprises a mixture of Bis-GMA and a glycol dimethacrylate.

10. A fluid dental composition according to any one of claims 1 to 9 characterised in that two dispersing agents are included, one to assist in dispersion of the fine particle size filler and the other to assist in dispersion of the large particle size filler of fillers.

11. A fluid dental composition according to any one of claims 1 to 10 characterised in that the dispersing agent for the fine particle size filler comprises a mixture of at least one organic phosphorus oxy-acid and a least one organic amine.

12. A fluid dental composition according to any one of claims 1 to 11 characterised in that the polymerisation catalyst is activated by visible light.

13. A fluid dental composition according to claim 12 characterised in that the visible light activated catalyst comprises at least one α-diketone and a least one organic amine capable of reducing the α-diketone when the latter is in an excited state.

14. A fluid dental composition according to any one of claims 1 to 11 characterised in that the catalyst comprises an organic peroxide and an organic activator for that peroxide.

15. A method for the production of a fluid dental composition as claimed in any one of claims 1 to 14 characterised in that it comprises forming dispersions of the fillers with their appropriate dispersing agents, non-polymerisable diluent and/or a portion of the polymerisable material and subsequently adding those dispersions to the bulk of the polymerisable material and removing any non-polymerisable diluent.

16. A package characterised in that it comprises two parts, one part containing a peroxide catalyst and the other part containing an activator for that catalyst, such that mixing of approximately equal quantities from each part produces a fluid dental composition according to claim 14.

Patentansprüche

1. Flüssige Dentalzusammensetzung, welche ein flüssiges polymerisierbares Material (A), einen Füllstoff (B), einen Polymerisationskatalysator für das polymerisierbare Material und ein Dispergiermittel enthält, dadurch **gekennzeichnet**, daß der Füllstoff aus einem Gemisch von anorganischen Füllstoffen besteht und in einem Volumenanteil von 60 bis 85% vorliegt, wobei der Volumenanteil ausgedrückt ist als

$$\frac{(\text{Volumen B} \times 100)}{(\text{Volumen A} + \text{Volumen B})}$$

daß das Gemisch von Füllstoffen einen feinteiligen Füllstoff und einen grobteiligen Füllstoff umfaßt, daß der feinteilige Füllstoff eine mittlere Größe in der längsten Abmessung von weniger als 0,1 µm aufweist und in einem Volumenanteil von 10 bis 55 % vorliegt, wobei der Volumenanteil ausgedrückt ist als

$$\frac{(\text{Volumen fein} \times 100)}{(\text{Volumen A} + \text{Volumen fein})}$$

und daß der grobteilige Füllstoff eine mittlere Größe in der längsten Abmessung von 0,5 µm bis 80 µm aufweist.

2. Flüssige Dentalzusammensetzung nach Anspruch 1, dadurch **gekennzeichnet**, daß der Volumenanteil des Füllstoffs 60 bis 75 % beträgt.

3. Flüssige Dentalzusammensetzung nach Anspruch 1 oder 2, dadurch **gekennzeichnet**, daß der Volumenanteil des feinteiligen Füllstoffs 10 bis 25 % beträgt.

4. Flüssige Dentalzusammensetzung nach einem der Ansprüche 1 bis 3, dadurch **gekennzeichnet**, daß der feinteilige Füllstoff aus kolloidalem oder gefälltem Siliciumdioxid besteht.

5. Flüssige Dentalzusammensetzung nach einem der Ansprüche 1 bis 4, dadurch **gekennzeichnet**, daß der grobteilige Füllstoff in seiner Teilchengrößenverteilung eine einzige Spitze zeigt.

6. Flüssige Dentalzusammensetzung nach einem der Ansprüche 1 bis 4, dadurch **gekennzeichnet**, daß der grobteilige Füllstoff in seiner Teilchengrößenverteilung zwei Spitzen zeigt.

7. Flüssige Dentalzusammensetzung nach einem der Ansprüche 1 bis 6, dadurch **gekennzeichnet**, daß das

flüssige polymerisierbare Material mindestens einen Diacrylat- oder Dimethacrylatester umfaßt.

8. Flüssige Dentalzusammensetzung nach Anspruch 7, dadurch **gekennzeichnet**, daß das flüssige polymerisierbare Material ein Gemisch von Vinylurethan und einem Glycoldimethacrylat umfaßt.

9. Flüssige Dentalzusammensetzung nach Anspruch 7, dadurch **gekennzeichnet**, daß das polymerisierbare Material ein Gemisch von Bis-GMA und ein Glycoldimethacrylat umfaßt.

10. Flüssige Dentalzusammensetzung nach einem der Ansprüche 1 bis 9, dadurch **gekennzeichnet**, daß sie zwei Dispergiermittel enthält, eines, welches die Dispergierung des feinteiligen Füllstoffs unterstützt, und eines, welches die Dispergierung des grobteiligen Füllstoffs oder der grobteiligen Füllstoffe unterstützt.

11. Flüssige Dentalzusammensetzung nach einem der Ansprüche 1 bis 10, dadurch **gekennzeichnet**, daß das Dispergiermittel für den feinteiligen Füllstoff ein Gemisch aus mindestens einer organischen Sauerstoffsäure des Phosphors und mindestens einem organischen Amin umfaßt.

12. Flüssige Dentalzusammensetzung nach einem der Ansprüche 1 bis 11, dadurch **gekennzeichnet**, daß der Polymerisationskatalysator durch sichtbares Licht aktiviert wird.

13. Flüssige Dentalzusammensetzung nach Anspruch 12, dadurch **gekennzeichnet**, daß der durch sichtbares Licht aktivierte Katalysator mindestens ein α-Diketon und mindestens ein organisches Amin, das zur Reduktion des α-Diketons fähig ist, wenn letzteres sich in einem erregten Zustand befindet, umfaßt.

14. Flüssige Dentalzusammensetzung nach einem der Ansprüche 1 bis 11, dadurch **gekennzeichnet**, daß der Katalysator ein organisches Peroxid und einen organischen Aktivator für dieses Peroxid umfaßt.

15. Verfahren zur Herstellung einer flüssigen Dentalzusammensetzung nach einem der Ansprüche 1 bis 14, dadurch **gekennzeichnet**, daß man Dispersionen der Füllstoffe mit ihren entsprechenden Dispergiermitteln, einem nichtpolymerisierbaren Verdünnungsmittel und/oder einem Anteil des polymerisierbaren Materials herstellt und anschließend diese Dispersionen zur Hauptmasse des polymerisierbaren Materials zugibt und gegebenenfalls nichtpolymerisierbares Verdünnungsmittel entfernt.

16. Packung, dadurch **gekennzeichnet**, daß sie zwei Teile umfaßt, einen Teil, der einen Peroxidkatalysator enthält, und einen anderen Teil, der einen Aktivator für den Katalysator enthält, wobei durch Mischen von annähernd gleichen Mengen eines jeden Teils eine flüssige Dentalzusammensetzung nach Anspruch 14 erhalten wird.

Revendications

1. Composition dentaire fluide, qui comprend une matière polymérisable liquide (A), une charge (B), un catalyseur de polymérisation pour la matière polymérisable et un agent dispersant, caractérisée en ce que la charge consiste essentiellement en un mélange de charges inorganiques en une fraction en volume de 60 à 85 %, la fraction en volume étant exprimée par le rapport

$$\frac{(\text{volume B} \times 100)}{(\text{volume A} + \text{volume B})}$$

ledit mélange de charges comprenant une charge en particules de petit diamètre et une charge en particules de grand diamètre, la charge en particules de petit diamètre ayant un diamètre moyen dans la direction la plus longue de moins de 0,1 µm et étant présente en une fraction en volume de 10 à 55 %, la fraction en volume étant exprimée par le rapport

$$\frac{(\text{volume des particules fines} \times 100)}{(\text{volume A} + \text{volume des particules fines})}$$

et la charge formée de grandes particules ayant un diamètre moyen dans la dimension la plus longue de 0,5 µm à 80 µm.

2. Composition dentaire fluide suivant la revendication 1, caractérisée en ce que la fraction en volume de la charge va de 60 à 75 %.

3. Composition dentaire fluide suivant la revendication 1 ou la revendication 2, caractérisée en ce que la fraction en volume de la charge en particules de petit diamètre va de 10 à 25 %.

4. Composition dentaire fluide suivant l'une quelconque des revendications 1 à 3, caractérisée en ce que la charge en particules de petit diamètre est de la silice colloïdale ou précipitée.

5. Composition dentaire fluide suivant l'une quelconque des revendications 1 à 4, caractérisée en ce que la charge en particules de grand diamètre présente un seul pic dans la distribution des diamètres de particules.

6. Composition dentaire fluide suivant l'une quelconque des revendications 1 à 4, caractérisée en ce que la charge en particules de grand diamètre présente deux pics dans la distribution des diamètres de particules.

7. Composition dentaire fluide suivant l'une quelconque des revendications 1 à 6, caractérisée en ce que la matière polymérisable liquide comprend au moins un ester diacrylique ou diméthacrylique.

8. Composition dentaire fluide suivant la revendication 7, caractérisée en ce que la matière polymérisable liquide comprend un mélange de vinyluréthanne et d'un diméthacrylate de glycol.

9. Composition dentaire fluide suivant la revendication 7, caractérisée en ce que la matière polymérisable comprend un mélange de bis-GMA et d'un diméthacrylate de glycol.

10. Composition dentaire fluide suivant l'une quelconque des revendications 1 à 9, caractérisée en ce que deux agents dispersants sont inclus, dont l'un contribue à la dispersion de la charge en particules de petit diamètre et l'autre contribue à la dispersion de la charge ou des charges en particules de grand diamètre.

11. Composition dentaire fluide suivant l'une quelconque des revendications 1 à 10, caractérisée en ce que l'agent dispersant pour la charge en particules de petit diamètre comprend un mélange d'au moins un oxyacide phosphoré organique et d'au moins une amine organique.

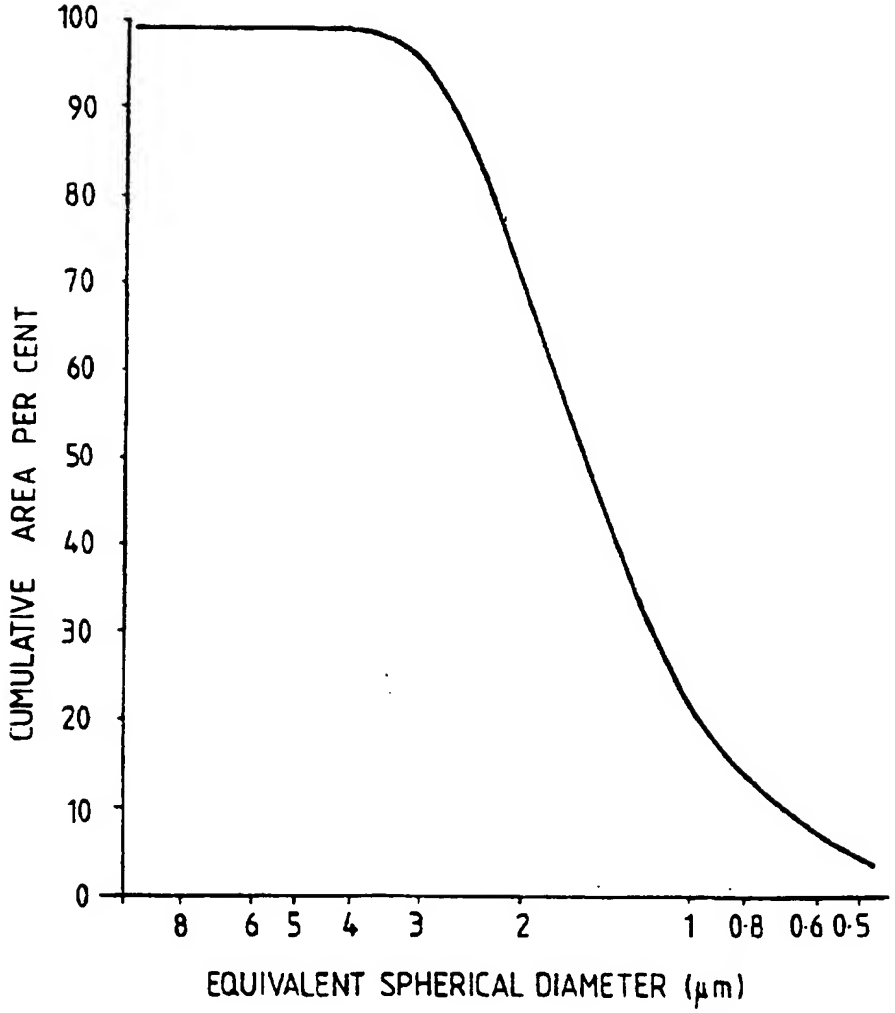
12. Composition dentaire fluide suivant l'une quelconque des revendications 1 à 11, caractérisée en ce que le catalyseur de polymérisation est activé par de la lumière visible.

13. Composition dentaire fluide suivant la revendication 12, caractérisée en ce que le catalyseur activé par la lumière visible comprend au moins une α-dicétone et au moins une amine organique capable de réduire l'α-dicétone lorsque cette dernière se trouve dans un état excité.

14. Composition dentaire fluide suivant l'une quelconque des revendications 1 à 11, caractérisée en ce que le catalyseur comprend un peroxyde organique et un activateur organique pour ce peroxyde.

15. Procédé de production d'une composition dentaire fluide suivant l'une quelconque des revendications 1 à 14, caractérisé en ce qu'il consiste à former des dispersions des charges avec leurs agents dispersants appropriés, un diluant non polymérisable et/ou une portion de la matière polymérisable et à ajouter ensuite ces dispersions à la masse de la matière polymérisable et à éliminer tout diluant non polymérisable.

16. Produit sous emballage, caractérisé en ce qu'il comprend deux parties dont l'une contient un catalyseur peroxydique et l'autre contient un activateur pour ce catalyseur, de manière que le mélange de quantités à peu près égales de chaque partie produise une composition dentaire fluide suivant la revendication 14.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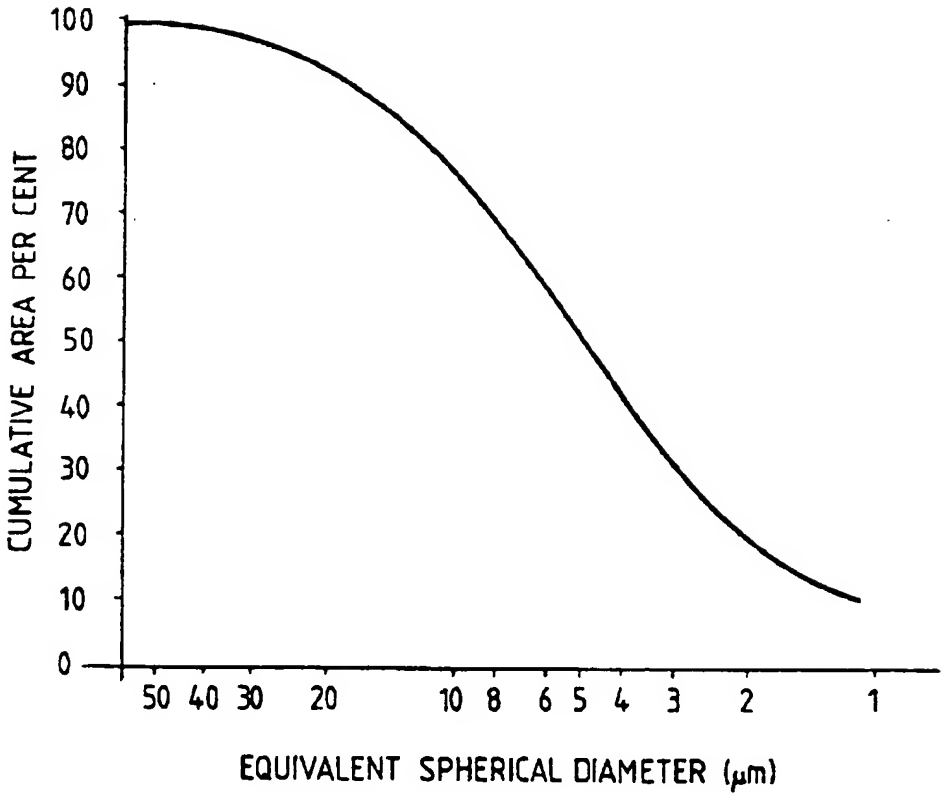
90
80
70
60
50
40
30
20
10
0
CUMULATIVE AREA PER CENT
8
6
5
4
3
2
1
0·8
0·6
0·5
EQUIVALENT SPHERICAL DIAMETER (μm)

Fig.1.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90
80
70
60
50
40
30
20
10
0
CUMULATIVE AREA PER CENT
50 40 30 20 10 8 6 5 4 3 2 1
EQUIVALENT SPHERICAL DIAMETER (μm)

Fig.2.